

Kinetics of hydrogen sulfide decomposition in a DBD plasma reactor operated at high temperature

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Abstract

The present study investigates the kinetics of hydrogen sulfide (H_2S) decomposition into hydrogen and sulfur carried out in a nonthermal plasma dielectric barrier discharge (NTP-DBD) reactor operated at ~ 430 K for in situ removal of sulfur condensed inside the reactor walls. The dissociation of H_2S was primarily initiated by the excitation of carrier gas (Ar) through electron collisions which appeared to be the rate determining step. The experiments were carried out with initial concentration of H_2S varied between 5 and 25 vol% at 150 mL/min (at standard temperature and pressure) flow rate in the input power range of 0.5 to 2 W. The reaction rate model based on continuous stirred tank reactor (CSTR) model failed to explain the global kinetics of H_2S decomposition, probably due to the multiple complex reactions involved in H_2S decomposition, whereas Michaelis-Menten model was satisfactory. Typical results indicated that the reaction order approached zero with increasing inlet concentration.

Key words

dielectric barrier discharge; hydrogen sulfide; kinetics; temperature

1. Introduction

Nonthermal plasma assisted direct decomposition of hydrogen sulfide to hydrogen and sulfur has become a subject of considerable investigation due to the resource utilization and hydrogen production [1]. Hydrogen sulfide (H_2S) is a byproduct in natural gas and oil refineries, which will be converted to sulfur in Claus process [2,3]. The major disadvantage of Claus process may be that valuable hydrogen (H_2) is wasted as water. On the other hand, hydrogen has a large number of applications, especially as a chemical feedstock, fuel and as an energy carrier [4]. Dielectric barrier discharge (DBD), as a variant of nonthermal plasma discharge (NTP) in which at least one of the electrodes is covered with a dielectric material, has been tested for various applications, especially for the abatement of various air pollutants [5–7]. The dielectric barrier limits the current flow in the discharge and prevents the formation of a spark/arc discharge. The dissipated electrical energy in DBD plasma is mainly transferred to energetic electrons, while the neutral gas remains close to ambient temperatures [5–7].

Over the past two decades, several researchers have investigated the kinetics of H_2S thermal decomposition either with

or without a catalyst [8–13]. In addition, H_2S decomposition was also tested with various plasma reactors [13–16]. However, most of these reports deal mainly with the conversion of H_2S , and the separation of products is one of the limiting points. The mechanism of H_2S decomposition reactions in NTP was investigated by several authors and it may be concluded that H_2S decomposition may be initiated by the excitation of carrier gas [17–19]. In our recent publication, kinetics of H_2S decomposition was discussed in a DBD reactor operated under ambient conditions [20]. As stated earlier, removal of sulfur deposited inside the reactor is warranted for practical applications. Hence, the scope of the present work is to elucidate the kinetics of H_2S decomposition in a DBD reactor operated at ~ 430 K.

2. Experimental

Conventional DBDs have been tested mainly for the dissociation of H_2S into hydrogen and sulfur, but not for the sulfur removal. For a continuous process, sulfur has to be removed from the reactor that can be achieved either collecting sulfur as a liquid or vapor. Even though sulfur melts at

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~ 392 K, the viscosity of the molten sulfur changes with temperature [21]. Efficient removal of sulfur would be possible at its minimum viscosity at ~ 430 K [22]. Therefore, experiments were carried out at ~ 430 K in the present study. The discharge was generated in a 50 cm length cylindrical quartz tube with an inner diameter of 20 mm, as shown in Figure 1. Copper wire wound on the outer surface of the quartz tube over a length of 15 cm acted as outer electrode, whereas a stainless steel rod was used as the inner electrode. The discharge gap between electrodes was 3.5 mm and the corresponding discharge volume was 27.2 cm^3 . The whole DBD setup was housed in an insulated vertical furnace as shown in Figure 1. An alternating current high voltage in the range between 10 to 22 kV at 50 Hz frequency was applied to create the discharge and the description of the apparatus and method of power measurement was given elsewhere [18,23]. Briefly an oscilloscope (Tektronix, TDS 2014 B) was used to measure the applied voltage of the system and the charge Q was measured by recording the voltage across a capacitor ($C = 1.5 \mu\text{F}$) connected series to the ground electrode and a V-Q Lissajous method was used to estimate the power dissipated in the discharge [23–26]. H_2S (diluted in argon) was introduced into the system through a Teflon tube, and a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector (TCD) was used to measure the conversion.

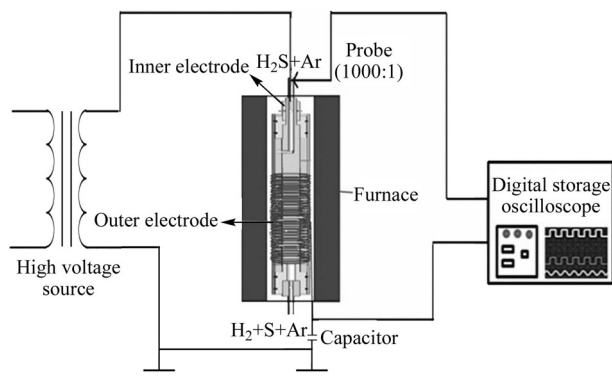


Figure 1. Schematic representation of dielectric barrier discharge reactor housed in furnace

3. Results and discussion

3.1. Conversion of H_2S in DBD plasma reactor operating at 430 K

The experimental results obtained from H_2S decomposition (5–25 vol% in Ar) in a DBD reactor at 430 K temperature are given in Figure 2. As seen from Figure 2, at any concentration H_2S conversion increased with increasing input power and lower H_2S concentrations (5 and 10 vol%) performed better. As seen from Figure 2, for 5 vol% H_2S , the conversion varied between 18% to 30% at input power limits between 0.55 and 1.13 W, whereas with increasing concentration to 25 vol%, the maximum conversion was only 12% at 1.92 W.

Even though the detailed mechanism of H_2S decomposition in NTP is still debated, often it is believed to be initiated by radicals whose number is higher than ions [19]. For H_2S diluted with argon gas mixture, the metastable $\text{Ar}(^3p_2)$ contributes to the dissociation of H_2S [27].

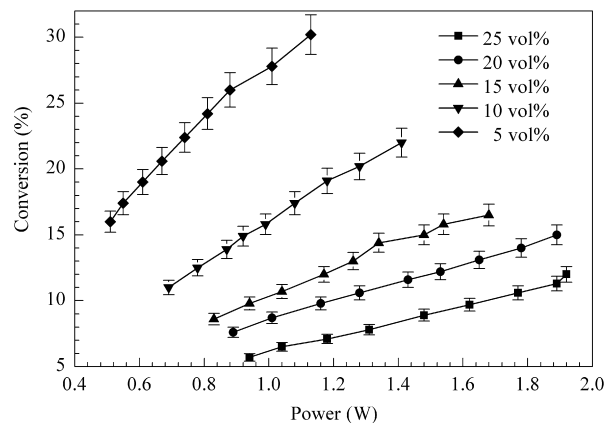


Figure 2. Conversion of H_2S as a function of power for different inlet concentrations (5–25 vol%) operated at 50 Hz frequency and at ~ 430 K

3.2. Kinetic study

The kinetic study of H_2S decomposition in NTP operated at ~ 430 K is presented here. The objective was to define a rate expression that allows modeling the reaction kinetics with experimental data. The approach followed is the same as the one for low temperature study [20]. The conversion results were obtained by varying the concentration and power at a frequency of 50 Hz at the discharge gap of 3.5 mm. This allowed the plot $X = f(P)$ for different inlet concentrations, as presented in Figure 3. Like in the case of room temperature study, the plot concludes that two parameters may be considered to establish the reaction rate, namely the inlet concentration and the power, and the conversion depends on the applied power. It has been observed that, at high concentrations the conversion was low and did not change significantly with concentration, whereas at low inlet concentrations, conversion changed significantly.

A differential reactor model (CSTR) was used to study the reaction order in the region of high concentrations (15, 20 and 25 vol%), where the conversion was around 15%. The mass balance of H_2S in a differential reactor may be written as following:

$$[C(\text{H}_2\text{S})_{\text{in}} - C(\text{H}_2\text{S})_{\text{out}}] \cdot q_v - r \cdot V = 0 \quad (1)$$

$$r = [C(\text{H}_2\text{S})_{\text{in}} - C(\text{H}_2\text{S})_{\text{out}}] \cdot \frac{q_v}{V} = \frac{C(\text{H}_2\text{S})}{\tau} \quad (2)$$

where, $C(\text{H}_2\text{S})$ is the fraction of hydrogen sulfide (liter of H_2S per liter of gas mixture) that flows in or out of the reactor respectively, q_v is the flow rate in liter per minute, V is the reactor volume in liter, r is the intrinsic reaction rate in liter of H_2S

per liter of gas mixture per minute and τ is the residence time of the gas. A power rate law was used to present the reaction rate:

$$r = k \cdot C(\text{H}_2\text{S})_m^n \quad (3)$$

where, k is the apparent rate constant, n is the reaction order and $C(\text{H}_2\text{S})_m$ is the mean value of inlet and outlet concentration. $C(\text{H}_2\text{S})_m$ instead of $C(\text{H}_2\text{S})$ has been used to minimize the error as $\sim 20\%$ which presents a high conversion to be treated as differential. The reaction order n was calculated by taking the logarithmic form of Equation (3):

$$\ln(r) = \ln(k) + n \cdot \ln C(\text{H}_2\text{S})_m \quad (4)$$

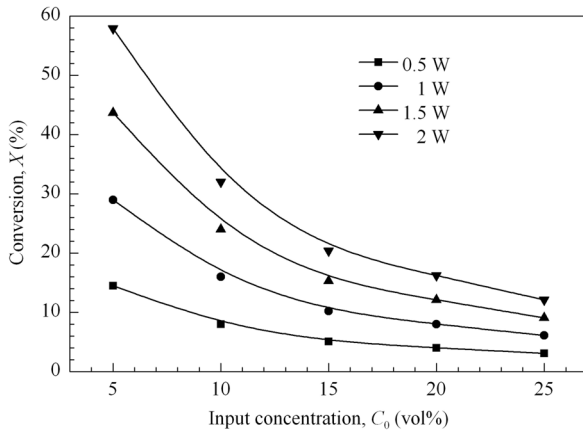


Figure 3. Conversion of H_2S as a function of the inlet concentration at different input powers (0.5–2 W) operated at 50 Hz frequency and at ~ 430 K

In Figure 4, $\ln(r)$ was plotted as a function of $\ln C(\text{H}_2\text{S})_m$. One can observe that the reaction order increased slightly from nearly zero to ~ 0.5 with increasing power from 0.5 to 2 W. The intercept $\ln(k)$ varied for each power but no relation to the power was seen as the reaction order was changing.

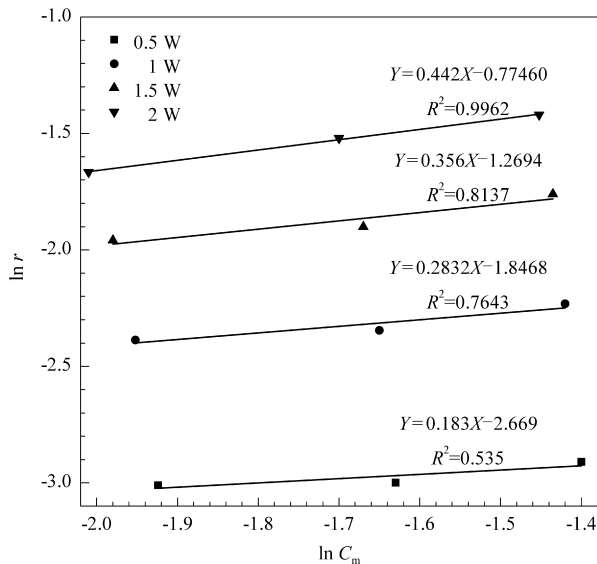


Figure 4. Determination of the reaction order for different power inputs

From the above study based on CSTR model, simple power rate law was not precise enough to describe the global kinetics. This result was expected due to the fact that, the mechanism of H_2S decomposition was composed of multiple complex reactions. Therefore another approach was applied to find out a rate model. As an alternative, a model similar to Michaelis-Menten kinetics was proposed. It was supposed that the reaction order could be increased from 0 to 1 by decreasing the inlet concentration. Such a behavior is known for enzyme catalyzed reactions, where the order decreases from 1 to zero with an increase in concentration. A similar equation as presented in Equation (4) was therefore adopted in which $-R$ is equal to the intrinsic reaction rate, $C_{\text{H}_2\text{S}}$ represents the inlet concentration and the model parameters a and b are shown in the following equation:

The above equation can be rewritten and integrated as follows

$$r = -R = \frac{a \cdot C_{\text{H}_2\text{S}}}{b + C_{\text{H}_2\text{S}}} \quad (5)$$

$$-R = \frac{a \cdot C_{\text{H}_2\text{S}}}{b + C_{\text{H}_2\text{S}}} = C_0 \frac{dX}{dt}$$

$$C_0 \int_0^X \frac{b + C_0(1-X)}{a \cdot C_0(1-X)} dx = \int_0^{t_R} dt = t_R = \tau$$

$$\tau = \frac{C_0}{a} X - \frac{b}{a} \cdot \ln(1-X)$$

$$a\tau = C_0 X - b \cdot \ln(1-X)$$

$$C_0 X = a\tau + b \cdot \ln(1-X)$$

$$C_0 = \frac{a\tau}{X} + \frac{b}{X} \cdot \ln(1-X) \quad (6)$$

The parameters a and b were determined by fitting in Equation (6) to the experimental data $X = f[C(\text{H}_2\text{S})_{\text{in}}]$ as seen in Figure 3. The rate expression proposed here presents an adequate model to describe the reaction kinetics similar to the results observed for room temperature activity [20]. The parameters a and b were plotted as a function of power (Figure 5 and Figure 6) and a linear increase of parameter a with power was observed (Figure 5). It was concluded that the parameter a can be seen as the apparent rate constant, $a = k_{\text{app}}$, which in its turn can be defined as:

$$K_{\text{app}} = k \cdot \eta e \quad (7)$$

$$\eta e = \alpha \cdot P \quad (8)$$

where, P is the power (W), η is a constant, k is the reaction rate constant and ηe is the concentration of electrons that is linearly proportional to the power.

So, finally the reaction rate can be written as:

$$-R = \frac{\alpha \cdot P \cdot k \cdot C_{\text{H}_2\text{S}}}{b + C_{\text{H}_2\text{S}}} \quad (9)$$

Figure 7 presents the rate of H_2S decomposition as a function of inlet concentration based on Michaelis-Menten model.

At low H_2S inlet concentrations, the excitation of Ar by electron collisions may be the rate determining step [17,19,20]. As seen in Figure 7, at low input power, as the number of excited Ar atoms is lower than the number of H_2S molecules, the conversion of H_2S may follow a zero order kinetics. With increasing power, the number of excited argon atoms may be higher than H_2S molecules and the reaction may follow first order with respect to H_2S concentration.

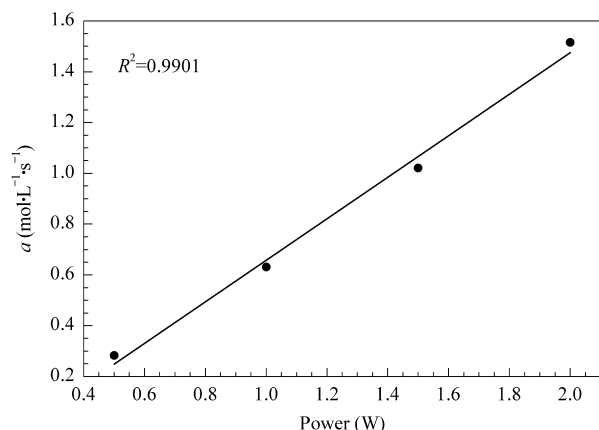


Figure 5. Parameter a as a function of power

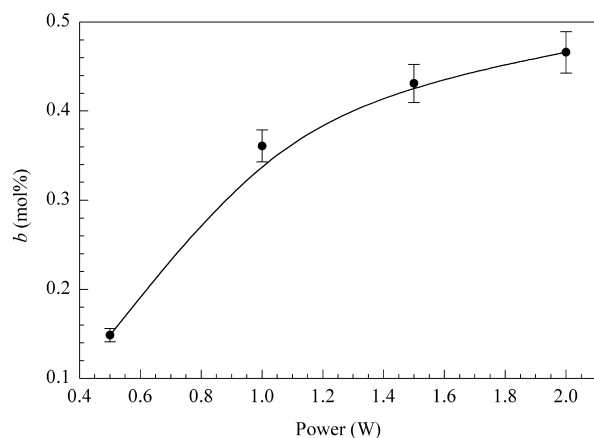


Figure 6. Parameter b as a function of power

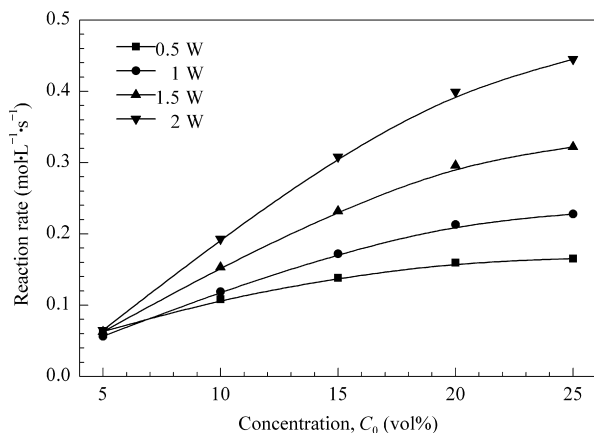


Figure 7. Reaction rate model fit to the experimental points, $X = f(\text{H}_2\text{S})$

As observed from the conversion data, at high H_2S concentration direct electron collision with H_2S became the dominant reaction [20], and the reaction order approached zero as the number of H_2S molecules remains higher than the number of excited species. At high H_2S concentrations, electrons may be captured by H_2S molecules that decrease the discharge current due to its electronegativity which decreases the conversion [17,20].

4. Conclusions

The kinetics of direct decomposition of H_2S into hydrogen and sulfur were studied in a nonthermal plasma DBD reactor operated at ~ 430 K for in situ removal of sulfur. It is observed that continuous stirred tank reactor (CSTR) model is applicable only for higher inlet H_2S concentrations, whereas, Michaelis-Menten kinetic model appears to be satisfactory for all the concentrations, where the reaction order varies from 1 to zero with increasing inlet concentration.

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